

REMARKS

Support for new claim 17 can be found, for example, on page 7 at lines 1-4. Support for new claim 18 can be found, for example, in Example 2 and table 2a. Support for new claim 19 can be found, for example, on page 5 at lines 21-22. Support for new claim 20 can be found, for example, in original claim 7 and on page 4 at lines 1-6. Support for new claim 21 can be found, for example, on page 4 at lines 11-24. Support for new claim 22 can be found, for example, on page 6 at lines 9-24. Support for new claim 23 can be found, for example, on page 6 at line 15. No new matter has been added.

Rejections under 35 USC §112

Claims 1 and 9 - 16 are rejected under 35 USC § 112.

The amendments to the claims render the rejections under 35 USC §112 moot. Thus, it is respectfully requested that the rejection under 35 USC §112 be withdrawn.

Rejections under 35 USC §103

Claims 1, 10 -14, and 16 are rejected as being unpatentable over Schrecengost (US 6,660,489) in view of Copeland (US 6,844,458), Grubbs (US 4,945,144) and Friswell (US 5,490,872).

Schrecengost teaches the determination of contaminants on a surface or in a food product via an ATP extraction method for biological samples. The reference provides no explanation for the meaning of biological sample and no specific food products are discussed.

The present invention detects unknown contaminants of low concentration in a hydrophobic/non-polar/non-ionic liquid matrix (e.g., fuel).

Food samples, such as disclosed in Schrecengost, are generally composed of organic compounds (e.g., proteins, fatty acids, sugars, salts, organic acids and water). Fuel is generally composed of great amounts of aromatic carbohydrates, and only contain water as a contaminant. Therefore, the conditions of Schrecengost's testing can not be compared with the method of the present invention, which is carried out in a "hydrophobic/non-polar/non-ionic liquid" sample.

Thus, the chemical and physical nature of the hydrophobic/non-polar/non-ionic liquid matrix of the present invention is entirely different in comparison to the food surfaces tested by Schrecengost.

The Examiner relies upon Copeland (US 6,844,458) to show that microbial contamination is found in crude vegetable oil and that vegetable oil is a hydrophobic matrix. See, Col. 2 at lines 25-39.

One skilled in the art would recognize that there are significant differences between vegetable oils and fuel oils. For example, vegetable oils are polar or comprise percentages of polar entities of at least about 8 - 15 % depending on the origin of the vegetable oil. See, for example, page 2 of Coconut Oil as Diesel Fuel vs. CarboDiesel by Diaz, July 2008; Fig 1 in Food Chemistry 110 (2008) 654-658; and Fig. 2 in Lipid Technology, Vol. 17, No. 5, 101 - 106) (copies attached).

In addition, vegetable oils are composed of triglycerides, which are unique for every species of plant oil. Triglyceride molecules consist of glycerol bound to three fatty acid molecules. Another important difference in chemical composition between fossil oil (e.g., fuel such as diesel or kerosene) and vegetable oil is the oxygen content. Vegetable oils contain from 10 - 12 % oxygen whereas fossil oils normally contain insignificant amounts of oxygen. Additionally, vegetable oils don't contain sulphur in contrast to diesel fuel. Furthermore vegetable oils, like coconut oil, don't contain any aromatic groups while mineral diesel typically contains 20 - 40 % aromatic compounds.

A skilled worker would have no expectation that a biological material dispersed or distributed in a vegetable oil would be the same as a hydrophilic compound or biological material dispersed or distributed in a hydrophobic/non-polar/non-ionic liquid sample. A skilled worker would also expect that the activity of an extractant in vegetable oil will be influenced by the chemical and physical nature of the oil (e.g., polarity of the oil, oxygen and sulphur content). Thus, the activity of an extractant in a hydrophobic/non-polar/non-ionic liquid matrix could not be predicted based upon the activity of an extractant in a vegetable oil.

The Examiner relies upon Grubbs (US 4,945,149) for its teaching regarding a cationic extractant, methylene blue. However, Grubbs does not cure the deficiencies of

Schrecengost or Copeland. Grubbs discloses a chemical reaction (i.e., polymerization of 7-oxan-orborene and its derivatives). Water is used as a solvent and methylene blue is used for complex building with polymers. In contrast to Grubbs, in the present invention dyes are added for an entirely different purpose, to visualize the aqueous phase and not to extract a hydrophilic component.

Friswell (US 5,490,872) discloses suitable markers for the tagging of petroleum, which are only visible if they are extracted in acidic aqueous solution. These markers are useful for the distinguishing of commercial aromatic liquids.

Calvo Salve (US5,843,509) is relied upon for its teaching that lecithin is a natural surfactant. Calvo Salve discloses the use of positively charged water-soluble polysaccharides and of a negatively charged phospholipid in a stabilized colloidal system.

Lawrence (US2002/0197631) discloses another method and device- for the analysis of biological samples.

Friswell (US 5,490,872), Calvo Salve (US5,843,509) and Lawrence (US2002/0197631) do not cure this deficiencies of Grubbs, Copeland and Schrecengost. They also do not teach or suggest a method for detecting a hydrophilic compound or biological material dispersed in a hydrophobic/non-polar/non-ionic liquid matrix.

Thus, based on the above remarks entry of this amendment and reconsideration of all the rejections is respectfully requested.

The Commissioner is hereby authorized to charge any fees associated with this response or credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,

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Some physical changes in Bajo Aragón extra virgin olive oil during the frying process

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Abstract

Changes of viscosity, transmittance spectra and colour of Bajo Aragón extra virgin olive oil, during the frying process, were studied, comparing them to the changes that occur during the frying process of high oleic sunflower oil. The studied oil was obtained from Empeltre variety olives. These changes, due to the deterioration of the oil during this process, were monitored by polar compounds measurement. Polar compounds content increased linearly with the frying cycle in both types of oil; however, the increase was faster in high oleic sunflower oil. The olive oil's transmittance spectra, after the frying process, proved that, not only do the peaks corresponding to the carotenoids and the chlorophyll disappear but also that transformation of the chlorophyll occurred. In high oleic sunflower oil spectra there were no changes. L^* and b^* colour parameters, measured on the CIELAB colour scale, showed the following behaviour: L^* values increased for olive oil after frying while the opposite happened for high oleic sunflower oil. In the case of the b^* parameter, the result was the same in both cases: when fried, more green and yellow colours appeared. The viscosity of both oils showed a non-linear increase with number of frying operations, which may correspond to a polynomial relationship. Despite their similar contents of oleic acid, olive oil was more stable to oxidation and there were some physical differences between the two types of oil.

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Keywords: Bajo Aragón; Empeltre; Olive oil; Frying; Potatoes

1. Introduction

The deep fat frying method, that is, the process in which food is cooked by immersion in hot oil, is considered to be the oldest and most common unit operation used in food preparation, especially in the mediterranean area. The aim of deep fat frying is to seal the food by immersing it in hot oil so that all the flavours and juices are retained within the crispy crust. The quality of the products cooked using this method depends not only on the frying conditions, such as temperature of the heated oil, frying time, food weight and frying oil volume, but also on the types of oil and the kind of food used (Varela, 1994). The chemical composition

of the frying oil and its physical and physicochemical properties also have an influence on the frying process. Usually many oils can be used for frying, e.g. palm oil, corn oil, cotton oil, soya oil and sunflower oil (Valenzuela, Sanhueza, Nieto, Petersen, & Tavella, 2003). Cottonseed, corn, peanut, and olive oils are used as a stable source of polyunsaturated fatty acids because of their low linolenic acid content (Boskou & Elmadfa, 1999). Since the most appropriate frying oil should be low in free fatty acids and polar compounds, extra virgin olive oil is a very interesting option when looking for a frying oil (Yaghmur, Aserrín, Mizrahi, Nerd, & Garti, 2001). There is a very notable production of olive oil in Spain and there are many different quality labels associated with the different olive varieties. In the region of Aragón, the quality label is "Bajo Aragón olive oil" and its source is the olives from the Empeltre variety.

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No studies have been reported about this extra virgin olive oil or its behaviour during the frying process.

During the frying process, there are many physicochemical changes in food as well as in oil (Valdés & García, 2006). The quality of frying oils worsens if it is used constantly. This is mainly due to three different factors: the moisture of food which may cause hydrolysis with free fatty acid formation; the atmospheric oxygen that enters the oil from the surface of the container (this factor increases the oxidative alteration) and the high temperature at which the operation takes place (a factor that results in thermal alteration). As a result of the deterioration, the oil sustains some physical changes: the colour darkens, the viscosity increases, and smoke appears (Paul & Mittal, 1997). Viscosity changes could be recorded by qualitative methods – *Viscofrit* – as well as by using viscometers and rheometers (Santos, Santos, & Souza, 2005). Colour changes could be tracked by spectrometric and colorimetric measurements.

The aim of this work is to determine how some physical parameters of extra virgin olive oil undergo changes during the frying process in comparison to high oleic sunflower oil. The variety of olive oil used for these experiments will be Empeltre. The frying process of this variety has not been studied. Research will mainly focus on the viscosity and colour.

2. Materials and methods

2.1. Materials

The following material was purchased at a local store: extra virgin Empeltre olive oil, high oleic sunflower oil and frozen potatoes.

2.2. Methods

2.2.1. GC analysis of the oils

Total fatty acids were transmethylated according to Frega and Bocci (2001). About two drops of olive oil were dissolved in six drops of a solution of 2 N KOH in methanol and then 2 ml of *n*-hexane were added. The mixture was vigorously shaken with a vortex for 2 min, sodium sulfate was added and the mixture was shaken again. The sample (0.4 µl) was injected 10 min later into a gas chromatograph (Hewlett–Packard 5890 CG) equipped with a split–splitless injector and a flame ionization detector. A DB-225, 30 × 0.25 mm ID and 0.15 µm column (J&W Scientific, Agilent) was used. The injector and detector temperatures were set at 250 °C. The oven temperature was kept at 190 °C for 1 min, then programmed from 190 °C to 210 °C at 4 °C/min, kept at 210 °C for 5 min, then heated from 210 °C to 215 °C at 3 °C/min and finally kept 18 min at the last temperature. Nitrogen was used as carrier gas at a flow rate of 1.0 ml/min.

The peak identification was carried out by comparing the peak retention time with those of the standard mixture. An internal standard was used for the quantification of

fatty acids. The GC response factor of each fatty acid was calculated by using the internal standard. The results were expressed as g fatty acid/100 g total fatty acids (%).

2.2.2. Performance of the frying process

Frying was performed on a domestic fryer (DeLonghi Easy Clean) at 170 °C with the food/oil ratio being 200 g/4l over about 3 min. The frying temperature was controlled using a probe joined to the thermometer.

2.2.3. Polar compound measurements

Measurement of polar compounds (in percentage) was done with a rapid method, that is, using a Testo 265 based on dielectric constant measurement. This instrument allows measurement from 40 °C to 210 °C and there is an interpretation that corresponds to every temperature. A number of frying cycles was done until the sensitivity limit of the instrument (23–24% polar compounds) was reached.

2.2.4. Viscosity measurements

A Bohlin CS–ETO stress controlled rheometer was used to measure the different oil viscosities. By this procedure, a concentric cylinder system is submerged in the oil and the force necessary to overcome the resistance of the viscosity to the rotation is measured. The viscosity value, in mPas, is automatically calculated on the basis of the speed and the geometry of the probe. Temperature (20 °C) was controlled with a water bath connected to the rheometer. The experiment was carried out by putting 3 ml of sample in a concentric cylinder system using 100 s^{−1} as shear rate.

2.2.5. Spectroscopic analysis and instrumental colour

The spectral and instrumental measurements of colour were done in olive oil and high oleic sunflower oil samples after filtration. For transmission spectra, a spectrophotometer, Avantes Ava Spec 1024, was used with a wavelength range from 380 to 780 nm at intervals of 2 nm and 1 cm width glass cuvettes, using hexane as a reference.

The CIELAB colour space (CIE, 1986) was studied after the spectra. Illuminant D65 was chosen as well as Observer CIE64. The following colour coordinates were determined: lightness (L^*), redness (a^* , red–green) and yellowness (b^* , yellow–blue). In addition, hue angle, which describes the hue or colour (h^*), was calculated ($h^* = \tan^{-1}(b^*/a^*)$) as was the saturation index or chroma (C^*) ($C^* = (a^{*2} + b^{*2})^{0.5}$) that describes the brightness or vividness of a colour.

3. Results and discussion

The Empeltre olive oil had a 69.8% oleic acid content and a 10.2% linoleic acid content in comparison to 57% for the oleic acid (usually 20–25% in normal sunflower oil) and 43% for the linoleic acid in high oleic sunflower oil (Table 1).

The aim was to establish a link between the fatty acid content and the oxidation stability during the frying pro-

Table 1
Principal fatty acid composition of the Empeltre olive oil and high oleic sunflower oil

Oil	Palmitic acid (%)	Stearic acid (%)	Oleic acid (%)	Linoleic acid (%)
Empeltre olive oil	16 ± 0.63	3.8 ± 0.3	69.8 ± 1.3	10.2 ± 0.6
High oleic sunflower oil	—	—	57 ± 0.9	43 ± 0.7

cess. In this sense, the rate of oxidation is proportional to the degree of insaturation (Paul & Mittal, 1997). Linoleic acid has two double bonds and for that reason, high oleic sunflower oil must be more susceptible to oxidation in the absence of antioxidants.

The polar compounds are a product of the oxidation and they are determined by a rapid method (Testo) in order to follow the life of the frying oil. Recently a good correlation of this method with the official one (by silica column chromatography) was established (Dobarganes, 2007). Fig. 1 shows the polar compounds content, depending on the frying number. In both oils there is a lineal behaviour with a very good correlation, although the degradation of high oleic sunflower oil occurs sooner, as expected, because of the fatty acid composition. Once the maximal sensitivity of the instrument was reached the experiments were stopped, that is, after the 60th frying process. Moreover, the limit established by the Spanish legislation for heated fats is 25% of polar compounds (Boletín Oficial del Estado, 1989).

There is a deterioration of the colour of oil during frying. According to Totani et al. (2006) one cause of this is the amino-carbonyl reaction between thermally oxidized oil and amino acids exuded by fried foods. Fig. 2 shows spectra of the frying oil at different numbers of frying operations. The shapes of the spectra in olive oil are very similar to those reported for other varieties of olive oil, Picual, Manzanilla, Lechín and Arbequina, submitted to an accelerated oxidation test (Ceballos, Moyano, Vicario, Alba, & Heredia, 2003). The first peak, at 450 nm, corresponds to a mixture of the chlorophylls and the carotenoids. The sec-

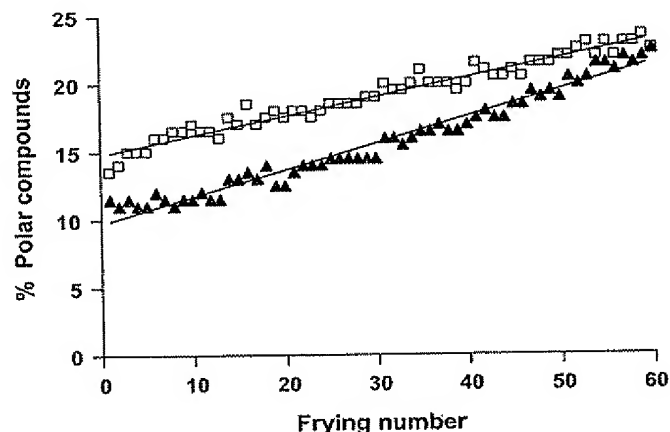


Fig. 1. Percentage of polar compounds depending on the frying number for olive oil (▲) and high oleic sunflower oil (□).

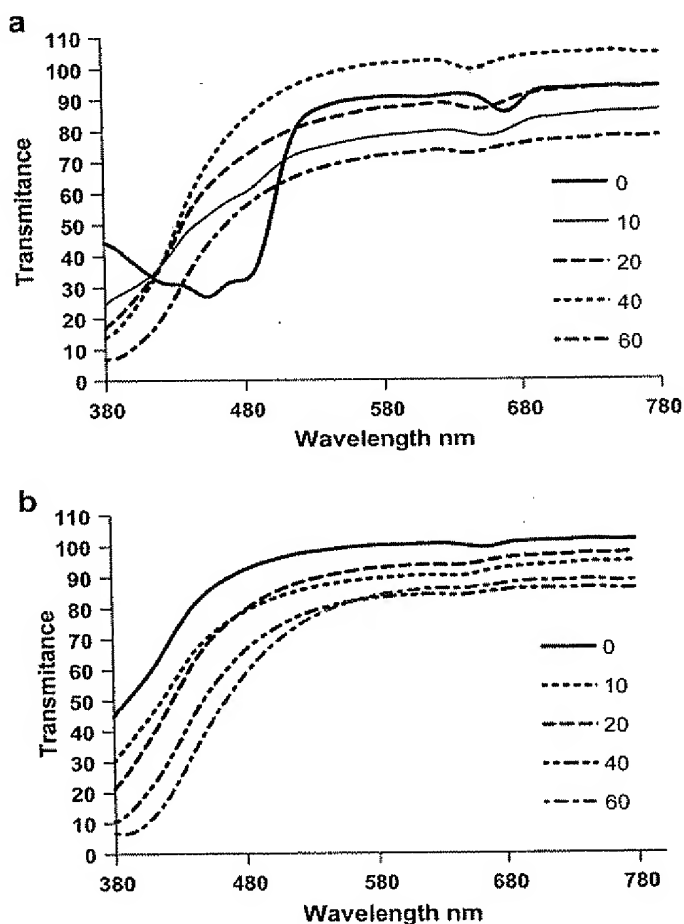


Fig. 2. Transmission spectra of olive oil (a) and high oleic sunflower oil (b) after the different frying cycles.

ond peak, at 483 nm represents the carotenoids responsible for the yellow colour of the oil. After frying, both peaks disappear as a result of the oxidation. Ndjouenkeu and Ngassoum (2002) proved that heating during frying leads to bleaching of palm oils, caused by the destruction of carotenoids responsible for their colour.

Another peak is seen at 666 nm, due to the chlorophyll. When the number of frying operations increases, the wavelength of this peak clearly changes. Such changes indicate the degradation of the pigment by loss of the magnesium of the molecule. The result of this degradation is a molecule of pheophytin (Guillén Sans, Yépez Pérez, Heredia Mira, & Guzmán Chozas, 1991). This last pigment provides a brown colour and it corresponds to the darker colour of the olive oil after frying. No maximal absorption appears

for refined high oleic sunflower oil, but only a slight inflexion above 665 nm and a shoulder at 415 nm, probably because the industrial extraction process destroys the pigments. The spectrum of this oil does not change too much after oxidation. Figs. 3 and 4 show the L^* and b^* values of the oils after frying. Lightness in olive oil showed slight increases with frying already proved by other authors (Guillén Sans et al., 1991). Sunflower oil lightness decreased with the frying cycle. In both oils, b^* values are positive, showing more yellow colour.

On the other hand, during deep-fat frying processing operations, the viscosity of the oil changes considerably with frying time and oil temperature (Bensmira, Jiang, Nsabimana, & Jian, 2007; Tsaknis & Lalas, 2002).

The results for viscosity of both frying oils are showed in Fig. 5. A two-phase graph can be found. Viscosity increases faster in the first step than in the second step. Probably, this is due to dimer formation. This graph can be fitted by a polynomial type. The increase of oil viscosity was attributed to polymerisation and formation of high molec-

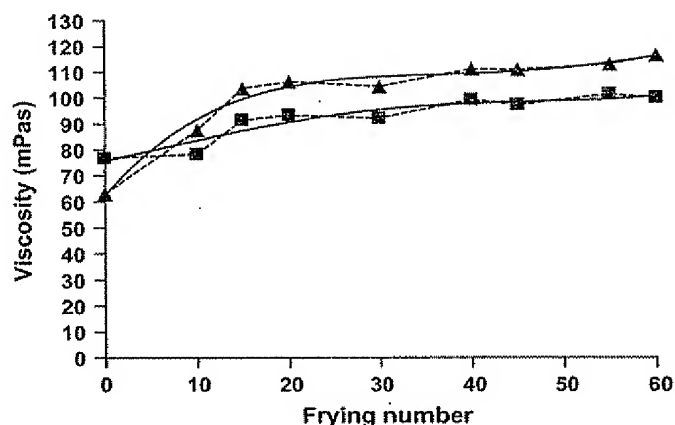


Fig. 5. Viscosity depending on the frying cycle for olive oil (▲) and high oleic sunflower oil (■).

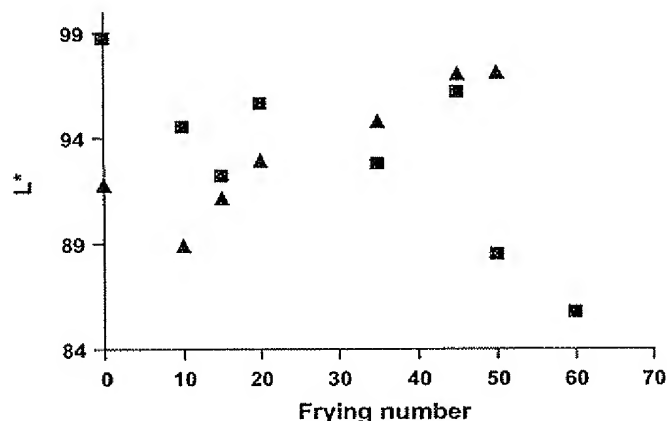


Fig. 3. L^* value depending on the frying cycle for olive oil (▲) and high oleic sunflower oil (■).

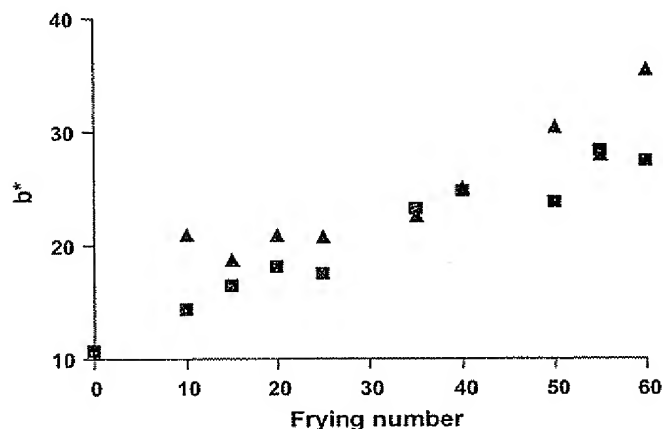


Fig. 4. b^* value depending on the frying cycle for olive oil (▲) and high oleic sunflower oil (■).

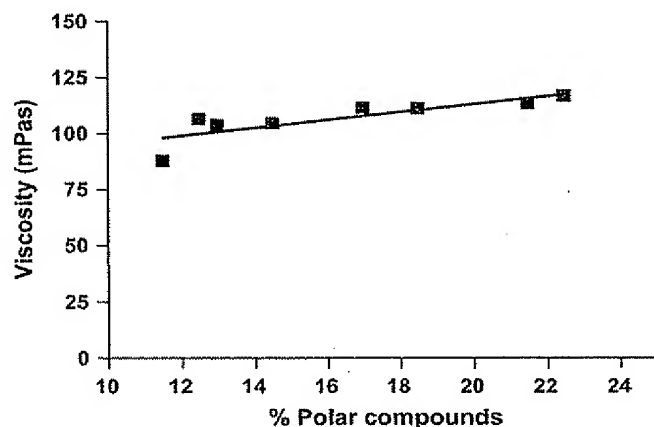


Fig. 6. Viscosity depending on the polar compounds for olive oil.

ular weight compounds (Stevenson, Vaisey-Genser, & Eskin, 1984). Similar results are described by Besbes et al. (2005) in oil from Deglet Nour and Allig seeds after thermo-oxidation.

In addition, viscosity values were highly correlated to polar compounds (Fig. 6). For this reason, viscosity measurements are a good index of oil degradation (Benedito, Mulet, Velasco, & Dobarganes, 2002).

In previous works, with different oils, such as *Moringa stenopetala* seed oil (Lalas, Gortzi, & Tsaknis, 2006), soybean oil (Farag & El-Anany, 2006; Jorge et al., 2006), palm, cottonseed and sunflower oils (Farag & El-Anany, 2006) vegetable oil blends (Fawzy-Ramadan et al., 2006) and unconventional oils (Mariod et al., 2006), the influence on the polar compounds, the colour and the viscosity that result from the frying process were studied. However, such influence has not been studied in the Empeltre olive oil. Our results (polar compounds) show a higher stability for Empeltre olive oil than for high oleic sunflower oil, as other authors have already reported (Chatzilazarou et al., 2006).

4. Conclusions

Bajo Aragón olive oil is very interesting during the frying process due to its fatty acid composition (it is a product rich in oleic acid) and oxidation stability, despite physical changes it undergoes during this operation.

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Biodiesel Featured Articles

Coconut Oil as Diesel Fuel vs Cocobiodiesel

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Abstract

Various global concerns such as the dwindling crude oil reserve, global warming and climate change, air pollution and public health, and more importantly the steady rise in the cost of fossil fuel, have altogether received rapidly growing interest in the use of renewable fuels (biofuels). For all diesel engines, alternative renewable fuels are vegetable oils referred to as bio-oils and transesterified bio-oil more popularly referred to as biodiesel. Biodiesel is a "diesel like" fuel which means it has properties very close to conventional diesel and can be used in land transport and stationary engines.

Medium speed diesel engines can operate well on the use of straight and unprocessed vegetable oil such as coconut oil. Compared to the use of biodiesel, vegetable oils will considerably reduce fuel cost in such engine.

As vegetable oils have differences in carbon chain composition, each oil must necessarily be evaluated separately. In most cases, however, vegetable oil specially coconut oil have been proven to be very clean fuels with excellent combustion properties.

Introduction

It is a fact that Rudolf Diesel invented the diesel engine in 1894 using peanut oil. This was a low-medium speed engine. The development of vegetable oil for the diesel engine did not prosper because oil companies came out with a much cheaper fuel which they called diesel fuel. In 1912, Rudolf Diesel stated *"the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time as important as petroleum and the coal tar products of the present time"*. That time is now.

A couple of decades back, several studies on the use of vegetable oils as fuels in diesel engines have been carried out. In the Philippines, the "coco-diesel" program was implemented in the mid-eighties using Coconut RBD oil assigning some bus companies for the pilot program. While the performance was promising, many experienced a relatively high pour point and cloud point problems. Problems with carbon deposits in the combustion chamber were also reported. The program was discontinued thereafter.

The development of renewable fuel for diesel engines in the Philippines have hibernated until the turn of the new millennium when cocobiodiesel was introduced jointly by the Asian Institute of Petroleum Studies, Inc (AIPSI) and the oleochemical companies (Senbel Inc. and Chemrez Inc.) to the United Coconut Planters Association (UCAP) and the Philippine Coconut Authority (PCA).

The growing global concern about environmental issues in the 90's (i.e. Clean Air Act) has increased the interest in alternative fuels paving the way to greater funding and effort for research studies. The increasing amount of greenhouse gases (ghg) such as CO₂ which is causing global warming and climate change, as well as the declining

reserves of fossil fuels, and more importantly, the high fuel prices have strongly increased the interest in the use of bio-oils and biodiesel for land transport and power generation.

Considering that the production cost of bio-oil and biodiesel is still higher than fossil diesel fuel, its use as a "neat" diesel replacement still pose a major problem. Fuel cost is often the largest part of the operating cost of transport operators and diesel power plants which directly correlates to profitability. Governments will, however, benefit from renewable fuels in terms of displacement of fuel imports.

Chemical Properties of Vegetable Oils

Vegetable oil like coconut oil consists of hydrocarbon called triglycerides. The triglyceride composition is unique for every plant oil. Triglyceride molecules consists of glycerol bound to three fatty acid molecules. Different plant oils have different compositions and there is no natural oil that consists of just one triglyceride type.

The different triglycerides have different properties and their coagulation point differ ("sebo" in Pilipino). That is why some triglycerides coagulate before others as they are cooled.

The oxygen content is the most important difference in chemical composition between fossil oils and vegetable oils. Vegetable oils contain 10 – 12% oxygen, whereas fossil fuel normally contain insignificant amounts of oxygen. The oxygen content affects both the specific energy and combustion properties of the oils. Vegetable oils specially coconut oil do not contain any sulfur in contrast to diesel fuel. If at all, only very small traces are found. Furthermore, coconut oil does not contain any aromatic groups while mineral diesel typically contain 20-40% aromatic compounds. Another important difference is that vegetable oils are polar compounds and have high lubricity feature for "boundary" lubrication of fuel injection pumps and injector nozzle units.

Brief on Coconut Oil

For many decades, coconut known as "tree of life", has been the preferred raw material for the production of soap and cosmetics. As food, coconut oil provides many health benefits being anti-viral, anti-bacterial, anti-fungal, anti-microbial and many more. This matter is extensively discussed by Dr. Bruce Fife in his book "the Coconut Oil Miracle". Dr. Fife points at the medium carbon chain specially lauric acid (C12) as the central point of its excellence. The following comparative Fatty Acid Profile of plant oils will show the significant features of coconut oil. Coconut oil as well as other plant oil consists of two (2) components – Glycerine and Fatty Acid.

Fatty Acid Profile ⁽²⁾ of Plant Oils (%)

Iodine Value ⁽³⁾	Coconut 7 - 10	Soybean 117 - 141	Rapeseed 105 - 120	Palm 44 - 54	Jatropha 100
Saturated Component :					
Caproic Acid (Saturated C _{6:0})	0.5	-	-	-	-
Caprylic Acid (Saturated C _{8:0})	8	Central point of the uniqueness of coconut oil			
Capric Acid (Saturated C _{10:0})	6				
Lauric Acid (Saturated C _{12:0})	47				
Myristic Acid (Saturated C _{14:0})	17.5	0.1	1	1	-
Palmitic Acid (Saturated C _{16:0})	9	11	2	39	15
Stearic Acid (Saturated C _{18:0})	3	4	1	5	6
Arachidic Acid (Saturated C _{20:0})	-	0.6	0.5	-	-
Behenic Acid (Saturated C _{22:0})	-	0.3	0.5	-	-
Total Saturated Component	91 ⁽⁵⁾	16	5	45	21
Unsaturated Component:					
Oleic Acid (Mono-unsaturated C _{18:1})	7	22	57	46	46
Linoleic Acid (Poly-unsaturated C _{18:2})	1.9	54	23	9	33
Linolenic Acid (Poly-unsaturated C _{18:3})	0.1	8	11	-	-
Gadoleic Acid (Mono-unsaturated C _{20:1})	-	-	2	-	-
Erucic Acid (Mono-unsaturated C _{22:1})	-	-	2	-	-
Total Unsaturated Component ⁽⁴⁾	9	84	95	55	79

Note: (2) Values taken from the Tribology Data Handbook

- (3) Iodine value is a measure of the level of unsaturated fatty acid. Low iodine number means low in unsaturated fat. Coconut has iodine value of only 7 - 10 which means it is highly saturated.
- (4) Medium Carbon Chain component of coconut oil. This group of carbon is also referred to as MCFA or medium carbon fatty acid in which most dominant is Lauric Acid or C₁₂. As health food, lauric acid is converted by the body into monolaurin which boosts the immune system.
- (5) Level of saturated component of coconut oil (91%) which indicates oxidation stability of coconut oil.
- (6) Unsaturated means that the carbon chain of a fatty acid is short of hydrogen making it reactive to oxidation and thus prone to bacterial growth. Mono-unsaturated has 1 carbon double bond in a carbon chain or short of 2 hydrogen. Poly-unsaturated has 2 or more double bonds or short of 4 or more hydrogen.

Coconut Oil as Diesel Fuel

The performance of vegetable oil as diesel fuel depends on the chemical composition of the plant oil particularly on the carbon chain length and the degree of saturation and unsaturation of the fatty acid molecules. Fatty acids that do not contain double bonds are referred to as saturated because they contain the maximum number of hydrogen that a carbon molecule can hold. Fatty acids that contain 1 double bond is called mono-unsaturated or is short of 2 hydrogen, while fatty acids with 2 or more double bonds are called mono unsaturated. Unsaturated fatty acids are prone to oxidation, bacterial growth, and formation of peroxides. Between these peroxides, cross-linking can occur and can cause oil polymerization and forms a plastic-like solids ("*nata*" in Pilipino). The greater the degree of unsaturation, the greater is its oxidation characteristic, bacterial growth, and peroxidation.

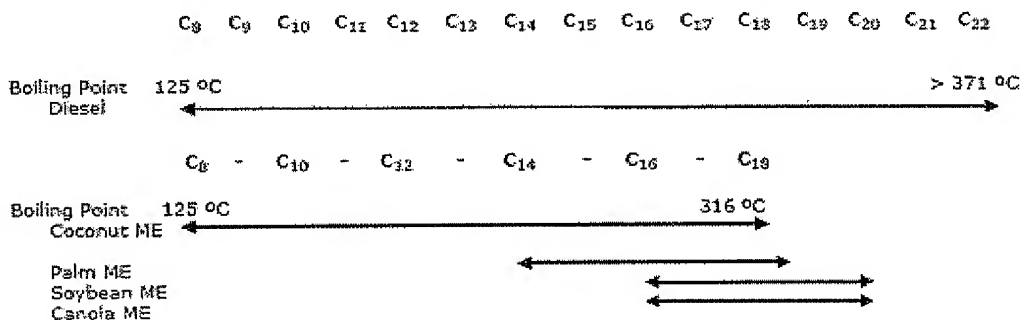
Problems related to this phenomenon can occur when vegetable oils are used as fuels for small high speed engines (such as luxury automobiles) which are more sensitive to kind of fuel and the fuel system.

Coconut Methyl Ester (or Cocobiodiesel)

In very simple term, Coconut Methyl Ester (CME) is coconut oil that has been converted to a diesel-like product. Plant oil has two main components known as glycerine and fatty acids. The fatty acid component has volatility feature similar to diesel. But in oil form, glycerine is attached to the fatty acid which causes the volatility of fatty acids to be suppressed. Glycerine has a high boiling temperature which is why plant oil makes excellent cooking oil. However, volatility is necessary for combustion when plant oil is used as fuel for internal combustion engines. It therefore necessitates the removal of glycerine.

The separation of glycerine from fatty acid is done by a reaction process known as esterification. Methanol is reacted with coconut oil with the aid of a catalyst to effect phase separation.. After a sufficient time of reaction, the methanol and glycerine are drawn out of the mixture leaving just the fatty substance known as methyl ester. Coco Methyl Ester is a diesel-like derivative of coconut oil. To a petroleum technologist, the fatty acid profile of coconut oil reveals a world of information specially when the oil is converted to various type of esters for lubrication, additive formulations, and other special applications :

First, when coconut oil is converted to a *diesel-like* product like methyl ester, its wide range of distillation from C8 to C18 becomes functional. Distillation range is the range of temperatures in which liquid transforms to vapor that becomes combustible with oxygen. Over 60 % of coconut oil constitutes medium saturated carbon that will provide good front-end distillation for better combustion and cold starting performance.



Second, the high level of saturation in coconut (91%) consisting mainly of "easy-to-burn" saturated medium carbon chain gives two (2) excellent benefits: 1) *oxidation stability* making coco methyl ester less prone to bacterial growth (a storage issue in other biodiesels), and 2) *high cetane number* which enhances combustion and acceleration response.

Third, the medium carbon fatty acids (MCFA) of coconut specially lauric acid (C12) has excellent solvency or solubility. Such feature makes CME a perfect biodiesel for developing countries like the Philippines where *old diesel engine* population comprises the majority. Old means heavy carbon deposits in combustion chamber and clogged fuel nozzles resulting in very inefficient combustion and high smoke emission. The solvency element of CME cleanses the fuel lines, decarbonizes the combustion chamber, and declogs the fuel nozzles to restore engine efficiency

Conclusion: (Maximizing the Benefit of Coconut Oil)

While the use of pure coconut oil is certainly feasible to run diesel engines specially if one is not very discriminating on its effect to engines, its use can be better maximized if it is converted to cocobiodiesel. First, the economics of cocobiodiesel in reducing fuel import

is far greater when used as diesel enhancer at 1% blend than when coconut oil is used as a 1 to 1 diesel substitute. Second, Clean Air is more extensively addressed in cocobiodiesel. Third, coconut oil is currently still more expensive than diesel fuel and there usually is very small production in relation to the annual demand for diesel fuel. Take note of the following comparison using Philippine data:

1. 70 million liters of Coconut oil used as 100% diesel substitute.

Direct Savings on fuel import :

$$70m \times P30 \text{ */liter} = P 2.10 \text{ billion/yr.}$$

2. 70 million liters of Cocobiodiesel used as 1% diesel enhancer

Direct Savings on fuel import

$$70m \times P30 \text{ /liter} = P 2.10 \text{ billion /yr.}$$

+ Indirect Savings from mileage economy**

$$635m \times P30 \text{ / liter} = P 19.0 \text{ billion /yr}$$

$$\text{Total Savings} = P 21.1 \text{ billion /yr}$$

* Import cost of diesel fuel is P30/ liter

** Biodiesel is registered as both diesel substitute and diesel quality enhancer with inherent features for solvency, lubricity, combustion improvement, and cetane number. A 1% blend can already restore fuel system efficiency and boost diesel fuel combustion resulting in mileage improvement. Quite a number of mileage tests show conservative mileage improvement of 10% from as little as 1% blend. This translates to a 9.1% reduction in fuel consumption. If this is a national average, reduction from the annual Philippine diesel demand of 7 billion liters is 635 million liters.

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Oil Absorption, Polymer and Polar Compounds Formation During Deep-Fat Frying of French Fries in Vegetable Oils

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INTRODUCTION

Deep-fat frying is one of the most commonly used methods for the preparation and manufacture of foods. One of the fundamental objectives of frying is to make the food more acceptable. When a food is fried, part of the moisture it contains is replaced by the frying fat. The fat that has penetrated into the food makes the food more palatable.

During deep-fat frying, the fat is continuously or repeatedly being exposed to temperatures of between 150°C-180°C in the presence of the substrate, air and water. Under these conditions, a complex series of reactions takes place; namely hydrolysis, oxidation, polymerization, isomerization and cyclization, resulting in the formation of both volatile and non-volatile products. These products affect sensory, functional and nutritional qualities of the frying oil or fat. Finally, as these reactions proceed, a point is reached where it is no longer possible to prepare high quality fried products and the frying oil or fat will have to be discarded from the fryer.

The result of deep-fat frying is a food with a distinctive structure consisting of outer and inner zones (Figure 1). According to several researchers (Robertson, 1978; Stevenson *et al.*, 1982; Gutierrez *et al.*, 1988), the surface area becomes crispy due to dehydration of the exterior parts

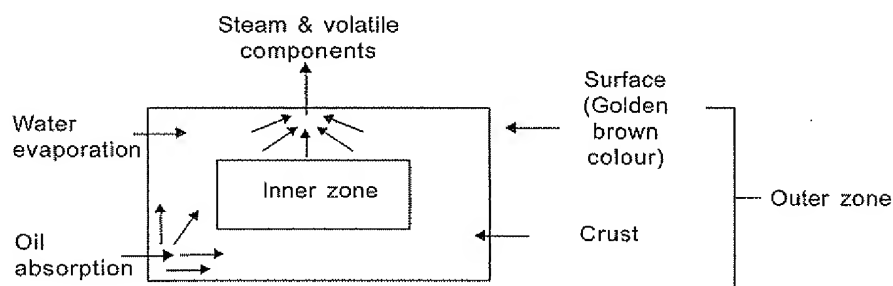
of the food during deep-fat frying. Its formation begins when the temperature of the frying medium is close to 100°C. The surface is generally an even, golden brown colour, resulting from the browning reaction that occurs when sugars and protein present in the substrate react in the presence of heat.

The crust is an area of numerous cavities, pores and large surface area, with a moisture content of less than 3%. The void created by the loss of water is largely filled by the absorption of the frying oil or fat. This absorbed fat exerts a tenderizing effect on the crust and contributes to the

flavour, aroma, lubricating and pleasant eating characteristics of the fried food. The core or the inner zone is a cooked moist interior composed solely of the food that is being fried. The texture and flavour changes occurring here are due to the effect of heat on the substrate rather than to fat absorption.

FAT ABSORPTION

The amount of frying oil or fat absorbed by a fried food depends on several factors. Among the important ones are the surface area of the food in contact with the frying medium, the moisture content or specific gravity of the food, the type of food, the ratio of the food crust to its core, the oxidative and heat stability of the oil/fat, the fryer design, whether frying is continuous or intermittent, the percentage



Source: Gutierrez *et al.* (1988).

Figure 1. Zones of fried food.

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replenishment with fresh oil, the duration of frying, the temperature of frying and the presence or absence of antioxidant.

Enormous quantities of palm oil/olein and palm shortening are now used for industrial production of snack chips, crackers, cookies, pastries, doughnut, pre-fried frozen French fries, instant noodle, fried chicken, fish fillet, meat nuggets and French fries (Masahi *et al.*, 1985; Yoon, 1991). It is thus of interest to know how much oil is absorbed by a particular fried product among the different frying oils/fats. Although fat absorbed by the fried food imparts a certain flavour and makes the food more palatable, a high oil pick-up could be a disadvantage to food processors as it will incur higher operating costs in replenishing the oil lost during the frying operation. A high fat content could also affect the shelf-life and stability of the food and may cause imbalance in the nutritive value between fats and non-fats such as carbohydrates and proteins.

A study which has been carried out by MPOB, investigated lipid absorption by a fried product, i.e. French fries, during batch or intermittent laboratory deep-fat frying in palm oil and palm olein versus soyabean and hydrogenated soyabean oils. This study was conducted with less than 10% replenishment of the fresh oils compared to 20%- 25% under normal practices and without shaking of finished food in the air. Hence, the results could differ from other studies. The polar and polymer contents and fatty acid compositions of fat extracted from the French fries as well as of oil collected from the fryers, were also assessed.

In the present investigation, frozen French fries were intermittently fried for 8 hr a day over five consecutive days at 180°C for 4 min in palm oil, palm olein, soyabean and partially hydrogenated soyabean oils respectively. Oil pick-up as well as

polymer and polar compound formation were studied.

FRESH FRYING OILS

The characteristics of the fresh frying oils used in the experiment and their fatty acid compositions are shown in Tables 1 and 2. As can be seen, of the four frying oils, soyabean oil has a very low resistance to oxidation (8 hr), as measured by the Rancimat. Its short induction period means it is not suitable to be used in deep-fat frying operations in fast-food chains, food manufacturing plants *etc.* where for economic, technical and nutritional reasons, a frying fat/oil needs to be stable for many hours, batches or days before being discarded from the fryer.

Under the French Food Law and Regulations (Firestone *et al.*, 1991), a fat/oil is considered unfit to be used as a deep-fat frying medium if it contains 2% or more linolenic acid (C18:3). Soyabean

oil and most soft oils are normally hydrogenated to reduce the level of linolenic and linoleic acids in order to improve their oxidative and heat stabilities and to eliminate fishy odours associated with linolenic acid.

Hydrogenation of the soya-bean oil reduces its linolenic acid content from about 9% to around 0.1% and increases its induction period by seven-fold to more than 58 hr. However, some 70% of the natural tocopherol is lost and about 41% of *trans* fatty acids are formed in comparison with the original oil. In Canada, the *trans* fatty acids are considered as equivalent to saturated fatty acids. According to Enig (1989), most *trans* fatty acids in hardened oils/fats have a straight chain structure much like saturated fatty acids and a typical hydrogenated commercial fat/oil in America contains as much as 42% *trans* fatty acids and 20% saturated fatty acids.

TABLE 1. CHARACTERISTICS OF FRESH FRYING OILS

Parameter	Palm oil	Palm olein	Soyabean oil	Hydrogenated soyabean oil
Colour (Lovibond, 51/4" cell)	2.2R 50 Y	1.9R 60Y	1.0R 16Y	1.0R 15Y
Free fatty acids (wt%)	0.06	0.04	0.03	0.02
Peroxide value (meq kg ⁻¹)	4.08	1.49	4.00	0.93
Anisidine value	2.96	1.89	2.28	2.92
Totox value	12.32	4.87	10.20	4.78
Slip melting point (°C)	37.0	20.0	-	35.8
Iodine value	52.0	56.1	135.1	73.9
Total tocopherol (ppm)	597	810	929	285
Induction period (Rancimat, hr, 100°C)	41.1	46.2	8.10	58.4
Polymer compounds (wt%)	0.62	0.47	0.84	1.04
Polar compounds (wt%)	7.96	7.84	5.89	5.20
Dielectric constant	0	0	0	0
Smoke point (°C)	214	216	217	219

TABLE 2. FATTY ACID COMPOSITION OF FRESH FRYING OILS (%)

Fatty acid	Palm oil	Palm olein	Soyabean oil	Hydrogenated soyabean oil
Lauric (C12:0)	0.2	0.3	0.1	0.2
Myristic (C14:0)	1.0	1.0	0.1	0.5
Palmitic (C16:0)	43.4	39.7	10.8	11.9
Palmitoleic (C16:1)	0.2	0.1	0.1	0.1
Stearic (C18:0)	4.4	4.2	3.7	7.5
Cis-oleic (C18:1c)	39.3	41.5	19.5	27.0
Trans-oleic (C18:1t)	Trace	Trace	Trace	39.8
Cis-linoleic (C18:2c)	9.8	11.3	54.4	1.8
Trans-linoleic (C18:2t)	Trace	Trace	Trace	1.1
Linolenic (C18:3)	0.2	0.2	9.0	0.1
Arachidic (C20:0)	0.4	0.4	0.3	Trace
Total trans	-	-	-	40.9
Others	0.7	0.9	0.6	9.9

Palm oil and palm olein are balanced fats containing about 50:50 saturated to unsaturated fatty acids (Table 2), the same ratio as found in human milk. They have marginal amounts of linolenic acids and about 10% linoleic acid (the essential fatty acid required by our body). They have a long induction period of more than 40 hr (Table 1), low levels of polymer compound (< 1%) and a high smoke point of over 200°C. These properties, coupled with their competitive price and consistent supply, palm oil/olein and palm shortening have over the last 20 years or so been a popular choice for food manufacturers in many countries, replacing (either totally or partially) traditional frying oils such as lard, tallow, peanut or cottonseed oil (Masahi *et al.*, 1985; Razali and Nor Aini, 1992).

FRENCH FRIES

The initial fat content of the pre-fried frozen French fries before frying was found to be around 5% while their moisture content varied between 64%-66%. After frying, some 32%-35% of the moisture was retained in the French fries. Table 3 shows the fatty acid composition of the oil extracted from the frozen French fry potatoes. The presence of 12% *trans* oleic acid means that

TABLE 3. FATTY ACID COMPOSITION OF OIL EXTRACTED FROM PRE-FRIED FROZEN FRENCH FRIES POTATOES BEFORE FRYING

Fatty acid	Percentage
Lauric (C12:0)	0.6
Myristic (C14:0)	0.9
Palmitic (C16:0)	32.0
Palmitoleic (C16:1)	0.1
Stearic (C18:0)	7.8
<i>Trans</i> -oleic (C18:1t)	12.0
<i>Cis</i> -oleic (C18:1c)	37.4
<i>Trans</i> -linoleic (C18:2t)	0.1
<i>Cis</i> -linoleic (C18:2c)	5.6
Linolenic (C18:3)	0.2
Arachidic (C20:0)	0.4
Others	2.7

the oil has been partially hydrogenated and may have been blended with palm oil as indicated by the high content of palmitic acid of 32%. Pre-fried frozen French fries imported by Malaysia from the western countries usually are pre-fried either in palm oil, animal fat or blend of palm oil with partially hydrogenated oil or hydrogenated soyabean oil.

The amount of oil picked up by the French fries during five days of frying is shown in Table 4. Starting with a fat content of roughly 5%, the oil absorbed by the French fries during the first two days of frying (equivalent to 16 hr and 28 batches) appeared to be similar for all oils with a narrow range of roughly 13%-14%.

Following an extended frying over five days, French fries fried in the soyabean oil contained a higher percentage (between 19%-21%) of oil than French fries fried in the other three oils. The soyabean oil contained a high proportion of linoleic acid (54%) and a substantial amount of linolenic acid (9%). These acids are extremely vulnerable to oxidation and also undergo thermal degradation to form polar and polymer compounds resulting in increased viscosity of the frying oil. According to Alim and Morton (1974), viscosity controls the amount of oil that coats a fried product and increases the oil absorption by the fried product. During five days of frying (Tables 5a and 5b) higher proportions of

TABLE 4. OIL ABSORPTION IN FRENCH FRIES (FF) DURING FIVE DAYS OF FRYING (%)

Days of frying (x 8 hr)	FF in palm oil		FF in palm olein		FF in soyabean oil		FF in hydrogenated soyabean oil	
	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
0	5.14	5.16	5.19	5.19	5.17	5.19	5.21	5.19
1	13.41	14.15	13.22	13.87	13.45	14.32	13.74	14.10
2	13.94	14.40	13.64	14.45	13.88	14.56	13.62	14.38
3	14.58	15.39	14.40	15.63	15.67	17.19	14.45	16.00
4	15.77	17.01	14.99	16.64	17.00	19.15	15.97	16.89
5	16.83	18.67	17.02	18.37	19.41	21.22	17.14	18.82

Notes:

Day 0 = Initial fat content of the frozen French potatoes.

Results are means of two replicates.

TABLE 5a. POLYMERIC COMPOUNDS IN FRYING OILS AND FRENCH FRIES (FF) DURING FIVE DAYS OF FRYING (%)

Days of frying (x 8 hr)	Palm oil		Palm olein		Soyabean oil		Hydrogenated soyabean oil	
	Oil	FF	Oil	FF	Oil	FF	Oil	FF
0	0.62	-	0.47	-	0.84	-	1.04	-
1	2.35	2.78	2.12	2.44	3.24	3.87	2.68	3.00
3	3.60	3.45	3.81	3.63	6.55	6.41	4.22	4.18
5	5.14	5.56	4.96	5.11	8.29	8.32	6.17	5.95

TABLE 5b. POLAR COMPOUNDS IN FRYING OILS AND FRENCH FRIES (FF) DURING FIVE DAYS OF FRYING (%)

Days of frying (x 8 hr)	Palm oil		Palm olein		Soyabean oil		Hydrogenated Soyabean oil	
	Oil	FF	Oil	FF	Oil	FF	Oil	FF
0	7.96	-	7.84	-	5.11	-	5.85	-
1	16.57	17.30	15.85	17.14	18.00	18.98	16.60	17.72
3	24.18	23.70	24.39	24.12	29.93	28.89	25.54	25.49
5	30.00	29.55	30.21	30.96	37.40	36.77	30.33	30.85

polar and polymer compounds were formed in the soyabean oil and as a result the French fries picked-up more of the polar and polymer compounds when fried in that oil, thus accounting for the higher percentage of oil absorbed.

The percentage of oil absorbed by the French fries each day varied partly because of variation in the initial moisture content of each batch of the pre-fried frozen French fries. Also, it was difficult to obtain a truly homogenous surface area to volume ratio from batch to batch. The presence of 5% fat in the frozen French fries before frying also contributed to higher oil pick-up. The actual fat pick-up by the French fries may have been reduced if shaking of the French fries had been carried out.

Shaking of the French fries in the air was said to be more effective (Greenfield *et al.*, 1984) in removing excess fat absorbed by the French fries than draining on an absorbent paper.

The changes in fatty acid composition of oil absorbed by the French fries as well as in the frying oils are shown in Table 6. Generally, the fatty acid profiles of each frying oil and the French fries fried in the oil were similar. As a consequence of deep-fat frying, *trans*-fatty acids were also formed. However, their levels in the non-hydrogenated oils and in the French fries were too low and would not really increase human intake of *trans* fatty acids as much as from the consumption of the French fries cooked in hydrogenated soyabean oil.

CONCLUSION

The oil absorption by the French fries fried in palm oil, palm olein and partially hydrogenated soyabean oil was approximately the same under the conditions studied. During five days of frying, the oil pick-up by the French fries increased in more or less the same proportion as the increase of polar and polymeric compounds in the three frying oils.

TABLE 6. CHANGES IN FATTY ACID COMPOSITION OF FOUR FRYING OILS AND FRENCH FRIES (FF) DURING FIVE DAYS OF FRYING (%)

a. Palm oil (PO)

Fatty acid	Palm oil				French fries			
	PO ⁰ initial	PO ¹	PO ³	PO ⁵	FF ⁰ initial	FF ¹	FF ³	FF ⁵
16:0	43.4	44.9	46.8	48.0	32.0	42.3	44.9	45.7
18:0	4.4	4.6	5.0	5.1	7.8	4.9	5.4	5.5
18:1c	39.3	38.6	37.7	37.4	37.4	39.1	38.0	37.9
18:1t	Tr	0.3	0.7	1	12.0	0.6	0.9	1.0
18:2c	9.8	8.4	6.4	5.9	5.6	9.5	8.4	7.1
18:2t	Tr	0.4	0.2	0.2	0.1	0.4	0.3	0.3
18:3	0.2	0.2	0.1	0.1	0.2	0.3	0.2	0.2
Others	2.5	2.6	2.8	2.2	4.9	2.9	1.9	2.3

b. Palm olein (POo)

Fatty acid	Palm oil				French fries			
	POo ⁰ initial	POo ¹	POo ³	POo ⁵	FF ⁰ initial	FF ¹	FF ³	FF ⁵
16:0	39.7	41	43.0	43.7	32.0	39.3	40.6	42.5
18:0	4.2	4.5	4.9	5.0	7.8	4.6	5.1	5.3
18:1c	41.5	41.2	40.8	40.3	37.4	41.9	41.2	41
18:1t	Tr	0.31	0.8	1.0	12.0	0.4	1.1	1.1
18:2c	11.3	10.0	8.0	7.4	5.6	11.0	9.0	8.6
18:2t	Tr	0.3	0.2	0.2	0.1	0.4	0.3	0.3
18:3	0.2	0.2	0.1	0.1	0.2	0.3	0.3	0.2
Others	2.6	2.5	2.2	2.2	4.9	2.1	2.4	2.0

c. Soyabean oil (SBO)

Fatty acid	Soyabean oil				French fries			
	SBO ⁰ initial	SBO ¹	SBO ³	SBO ⁵	FF ⁰ initial	FF ¹	FF ³	FF ⁵
16:0	10.8	11.7	13.2	13.4	32.0	12.9	13.1	13.8
18:0	3.7	3.9	4.3	4.4	7.8	3.9	4.3	4.5
18:1c	19.6	20.6	21.8	22.0	37.4	21.1	21.7	22.3
18:1t	Tr	0.4	0.8	1.3	12.0	0.8	1.6	1.7
18:2c	54.4	52.4	50.7	49.8	5.6	50.7	48.3	47.3
18:2t	Tr	0.3	0.5	0.3	0.1	0.5	0.5	0.5
18:3	9.0	8.4	7.5	6.8	0.2	7.5	7.2	6.8
Others	2.3	2.1	2.6	1.9	4.9	2.6	3.3	3.0

d. Partially hydrogenated soyabean oil (PHSBO)

Fatty acid	PHSBO				French fries			
	PHSBO ⁰ initial	PHSBO ¹	PHSBO ³	PHSBO ⁵	FF ⁰ initial	FF ¹	FF ³	FF ⁵
16:0	11.9	12.6	14.0	14.7	32.0	12.8	14.4	15.3
18:0	7.5	7.5	7.6	7.8	7.8	6.9	7.5	7.7
18:1c	27.0	28.3	30.9	30.9	37.4	20.5	20.8	21.2
18:1t	39.8	37.8	35.4	34.3	12.0	42.8	42.0	38.0
18:2c	1.8	1.8	1.2	1.1	5.6	3.8	2.2	1.7
18:2t	1.1	1.1	0.8	0.8	0.1	2.2	2.0	1.8
18:3	0.1	0.1	0.1	Tr	0.2	0.5	Tr	Tr
Others	11.8	12.1	11.1	11.1	4.9	10.5	11.1	14.3

However, during five days of frying, French fries fried in soyabean oil generally absorbed more fat in comparison to French fries cooked in the other three oils. The difference in the fat absorption was partly due to the higher polar and polymeric compounds formed in the soyabean oil and subsequent higher absorption by the French fries.

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